CHAPTER 1

INTRODUCTION

1.1 General Information

Nowadays, the global warming issue getting crucial. This issue happened due to the atmospheric carbon dioxide (CO_2) growth rapidly from human being. Greenhouse gases are the main factor which causes the global warming. In the greenhouse gases, there is 72% of totally emitted CO_2, 18% of methane (CH_4) and 10 % of nitrous oxide (NO_X). CO_2 are the most important cause of global warming. CO_2 is inescapably created by burning fuels like e.g. natural gas, dieses, organic diesel, petrol and oil. International Panel on Climate Change (IPCC) predicted that atmospheric CO_2 level could reach up to 590 ppm by 2100 and the global mean temperature would rise by 1.9 °C (Li, An, Park, Majeda & Tang, 2014). The greenhouse gases will seriously impact in many different aspects, such as ice melting at the Earth's pole, fast rising sea level and increasing precipitation across the globe. CO_2 molecule is very stable which is not easily transformed into others chemical in a reaction. By using a photocatalyst, CO_2 can be served as a building block for the synthesis of other useful chemicals and chemical intermediates.

The photocatalyst for the conversion of carbon dioxide (CO_2) into hydrocarbon fuels with the visible light energy is a promising and eco-friendly approach to prevent the increase in greenhouse gases and exhaustion of fossil resources. Among the semiconductor materials like Titanium dioxide (TiO_2), Zinc oxide (ZnO), Tungsten oxide (WO_3) and Zinc Sulphide (ZnS), TiO_2 is one of the most promising photocatalyst due to its versatile characteristics including non-toxicity, low cost, high photocatalytic and chemical biologically inert. From the TiO_2 materials, TiO_2 nanoparticles are great interest in photocatalytic properties, hence it is used in antiseptic and antibacterial compositions. Furthermore, it is also been used in many application such as degrading organic contaminants and germs, UV-resistant material, manufacture of printing ink, self-cleaning ceramics and glass, coating. Nevertheless, TiO_2 nanoparticles also used in making of cosmetic products such as sunscreen creams, whitening creams, morning and night creams, skin milks and in the paper industry for improving the opacity of paper.

However, the photocatalytic activity of TiO_2 is limited by its low capability of absorption in the visible light and fast recombination rate of the photogenerated electron-hole pairs. The wide band gap (3.2 eV for anatase and 3.0 eV for rutile) of TiO_2 only can excited in UV range of spectrum ($\lambda < 380$nm). It covers only ~ 5% of the whole solar spectrum compare to the visible light spectrum (Sim, Leong, Phichiah & Shliza, 2015). Various studies have been carry out to improve the photocatalytic activity of TiO_2 by doping with noble-metals and non-metals. Besides, TiO_2 can be coupled with semiconductors. The noble metal such as gold (Au), silver (Ag), and copper (Cu), possess a great ability of visible light absorption due to existence of localized surface plasmon resonance (LSPR). LSPR is an optical phenomena which generated by light when it contact with conductive nanoparticles (NPs) that smaller than incident wavelength. As in surface plasmon resonance, the electric field of incident light can be deposited to collectively excite electrons of a conduction band, with the result being coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, dielectric environment and separation distance of NPs (Eleonora petryayeva, Ulrich J.krull, 2011). Moreover, noble metal will transfer the electron to TiO_2 and traps the electron in the metal TiO_2 nanostructures to minimize the surface charge recombination in TiO_2.

Further studies have been devoted to improve the optical absorption and increase the charge carrier transport Reduced graphene oxide (RGO) was used in the hybrids thus diminish the bandgap and minimize the electron-hole recombination rate. Graphene is a two-dimensional sp^2-hybrized carbon nanosheet which consist rich characteristic including high specific surface area, high electron mobility and tunable band gap. Liang et al. prove that the less deficient graphene-TiO_2 nanocomposite thin film resulted in larger improvement of photocatalytic for the photoreduction of CO_2 to CH_4. Tan et al. described that graphene-TiO_2 nanocomposite adopt the ultraviolet light (UV) produce a maximum CH_4 product yield of 0.135μmol g cat^{-1} h^{-1}, which is 2.1 and 5.6 fold higher than graphite oxide and pure anatase. These studies have shown that the enhancing effects of graphene on the photocatalytic of TiO_2 in hybrid materials.

Recent years, research shows that the graphene-TiO_2 nanocomposite is limited to photodegradation of organic pollutants. This encourages people to do more research toward the photocatalytic conversion of CO_2 to CH_4 with the assist of RGO as the proficient electron trapper to overwhelm the recombination of photoinduced electron-hole pairs.

1.2 Problem Statement

Nowadays, the issue of the CO_2 cause the global warming getting serious. CO_2 are the highest gases which contains around 72% of the greenhouse gases. This mean that CO_2 are the most important cause of global warming compare to another two gases (18% of CH_4 and 9% of NOx). CO_2 is inescapably created by burning fuels like e.g. natural gas, diesel, organic- diesels, petrol and oil. The emission of CO_2 have been increase dramatically within the last 50 years and still increase by almost 30% each year. The CO_2 is released to the atmosphere where it remain for 100 to 200 years. This lead the concentration of CO_2 in atmosphere increase, hence the earth temperature increase. The CO_2 gives the serious impact in different aspect such as ice melting at the Earth's pole, fast rising sea level and increasing precipitation across the globe (Li, An, Park, majeda & Tang, 2014).

Most of the photochemistry and photoelectrochemistry process involves the excitation of TiO_2 by photon with light energy greater than energy gap. However, the wide band gap (3.2 eV for anatase and 3.0 eV for rutile) only can excited with UV light which covers ~ 5% of the irradiation ($\lambda < 380$ nm) from the total solar spectrum. The solar spectrum consists of ~ 43% of the visible light and the remaining ~52% is infrared light. The availability of UV spectrum is marginal in comparison to the visible light spectrum. Hence it causes a major limitation of utilizing the UV source for its natural activation. Thus the present available TiO_2 is not suitable for the utilization of visible spectrum of solar energy. Therefore, the employment of solar energy for a photocatalytic process can be improved by altering the energy gap response of TiO_2 to the visible light region (Yu, Zhang, Cheng, & Su, 2007).